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ARTICLE

Isolation of a Series of Uranium Organophosphinates

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A new series of uranium organophosphinates has been hydrothermally synthesized by using hydroxymethyl phenylphosphinic acid (HMPPA, HL) in the presence of imidazole derivatives, namely $\text{UO}_2(\text{L})_2$ (**HMPP-U1**), $(\text{UO}_2)_2(\text{L})_4(\text{dib})$ (**HMPP-U2**), $(\text{UO}_2)_2(\text{L})_2(\text{ox})(\text{dib})$ (**HMPP-U3**), $(\text{Hbpi})_2[(\text{UO}_2)_4(\text{L})_6(\text{ox})_2]$ (**HMPP-U4**) and $(\text{UO}_2)_2(\text{L})_2(\text{ox})(\text{bpbi})_2$ (**HMPP-U5**) (ox = oxalate, dib = 1,4-di(1H-imidazol-1-yl)benzene, bpi = 1-(biphenyl-4-yl)-1H-imidazole, bpbi = 1-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole). **HMPP-U1** was directly synthesized through hydrothermal reaction between HMPPA and UO_2^{2+} , featuring a single chain structure constructed from sole UO_6 tetragonal bipyramids bridged by HMPP ligands. Further introduction of imidazole derivatives, a layered structure of **HMPP-U2** is formed, in which dib molecules are coordinated to uranyl centers as bidentate coligands. By adding glycol into the synthesis, a common dimeric building unit is isolated, which comprises two U-centered pentagonal bipyramids linked by in-situ generated oxalate group. In **HMPP-U3**, one-dimensional structure comprising such dimeric uranyl entities and HMPP ligands is pillared by dib, forming a layered assembly. **HMPP-U4** incorporates the dimeric uranyl units connected by HMPP ligands, leading to a two-dimensional arrangement with bpi as the template. **HMPP-U5** features a one-dimensional structure formed by the uranyl diemrs and HMPP ligands. The bpbi molecules serving as coligands are coordinated to the chain. The syntheses, structure as well as the correlations and discrepancies of these uranyl organophosphinates have been discussed in this paper.

Introduction

In recent years, uranyl organic coordination polymers have received growing attentions due to their fascinating structure diversities¹⁻⁸ and potential applications in ion exchange,⁹ proton conductivity,¹⁰ photochemistry and especially the tremendous importance of U(VI) in the nuclear energy cycle.¹¹ To obtain novel uranyl organic coordination polymer materials, various carboxylate and phosphonate ligands are the primary selection for their moderate or strong ligation.^{12,13} As the rich structural diversities of uranium chemistry, we have been working on the study of uranium complexes including carboxylates, phosphonates, arsonates and sulfonates.¹⁴ In our recent work, a series of aromatic and aliphatic phosphonate ligands have been utilized to isolate uranyl complexes.^{14a,14b} Phosphonate group (PO_3) possesses three oxygen atoms, which can coordinate metals in any state of protonation. In contrast to phosphonates, organophosphinates ($\text{R}_1\text{PO}_2\text{R}_2$) have been less investigated. Although the phosphinate group contains less oxygen donor atoms capable of bonding to metals compared with corresponding phosphonate group, a better modulation and adjustment of the additional substituent allow differently related organophosphinic acids to be interesting agents on the construction of new metal-organic coordination hybrids. For example, a series of transition metal coordination polymers with (2-carboxyethyl)(phenyl)phosphinate as the ligands has been successfully synthesized in recent years.¹⁵ However, a study on the synthesis of actinide organophosphinates is rather

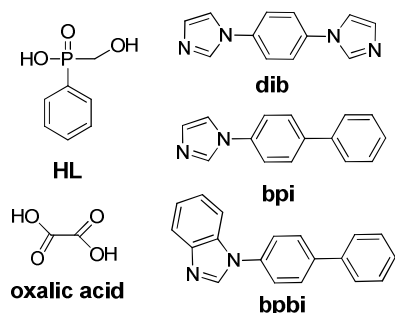
rare.¹⁶⁻¹⁸ To the best of our knowledge, only three uranium-bearing compounds were reported, including two oligomers^{16,17} and one linear-chain uranyl organophosphinates.¹⁸ It is a very challenging task to obtain new actinide phosphinates with versatile architectures.

In this study, (hydroxymethyl)(phenyl)phosphinic acid (HMPPA), which has never been used for construction of metal-organic hybrids, was selected as the candidate for synthesizing uranyl complexes. In order to further enrich uranyl organophosphinate structures, auxiliary N-donor ligands are adopted in this contribution. These basic imidazole species could serve as co-ligands, space fillings or charge compensators. The phosphinate and N-contained organics may have effects on the connection between the uranium ions and the organic ligands in the structure, as well as on charge density distribution, thus novel architectures could be induced. In this paper a brand-new series of uranyl organophosphinates are described and discussed: $\text{UO}_2(\text{L})_2$ (**HMPP-U1**), $(\text{UO}_2)_2(\text{L})_4(\text{dib})$ (**HMPP-U2**), $(\text{UO}_2)_2(\text{L})_2(\text{ox})(\text{dib})$ (**HMPP-U3**), $(\text{Hbpi})_2[(\text{UO}_2)_4(\text{L})_6(\text{ox})_2]$ (**HMPP-U4**) and $(\text{UO}_2)_2(\text{L})_2(\text{ox})(\text{bpbi})_2$ (**HMPP-U5**) (ox = oxalate, dib = 1,4-di(1H-imidazol-1-yl)benzene, bpi = 1-(biphenyl-4-yl)-1H-imidazole, bpbi = 1-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole).

Experimental section

Materials and methods

All chemicals were purchased commercially and used without further purification. The ligands and imidazole derivatives used in this work are listed in Scheme 1. The elemental analyses of C, H, and N were conducted on a Perkin–Elmer 2400 elemental analyzer. Infrared spectra were collected from single crystals of all the uranyl organophosphinates using a Nicolet 6700 FT-IR spectrometer. The spectra were collected with a diamond ATR objective. Powder X-ray diffraction (PXRD) patterns were performed on a D8 Focus (Bruker) diffractometer with Cu-K α radiation Field-emission ($\lambda = 0.15405$ nm, continuous, 40 kV, 40 mA, increment = 0.02°).



Scheme 1. A schematic representation of the phosphinate and oxalate ligands as well as imidazole derivatives.

Synthesis of $(\text{UO}_2)_2(\text{L})_2$ (HMPP-U1)

A mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50 mg, 0.1 mmol), HMPPA (34 mg, 0.2 mmol), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (20 μL) and deionized water (1.5 mL) was loaded into a 20-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160°C for 2 days, and then cooled to room temperature naturally, initial pH 1.0, final pH 2.0. Yellow rod-like crystals were isolated. PXRD pattern proves the phase purity (Figure S1). Elemental analysis observed (Calcd): C 27.56% (27.46%); H 2.72% (2.63%).

Synthesis of $(\text{UO}_2)_2(\text{L})_4(\text{dib})$ (HMPP-U2)

A mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50 mg, 0.1 mmol), HMPPA (34 mg, 0.2 mmol), dib (20 mg, 0.1 mmol) and deionized water (1.5 mL) was loaded into a 20-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160°C for 3 days, and then cooled to room temperature naturally, initial pH 1.0, final pH 1.5. Yellow block crystals were isolated. PXRD pattern is shown in Figure S2, proving the phase purity. Elemental analysis observed (Calcd): C 33.28% (33.49%); H 2.82% (2.95%); N 3.98% (3.91%).

Synthesis of $(\text{UO}_2)_2(\text{L})_2(\text{ox})(\text{dib})$ (HMPP-U3)

A mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50 mg, 0.1 mmol), HMPPA (17 mg, 0.1 mmol), dib (10 mg, 0.048 mmol), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (20 μL), glycol (0.5 mL) and deionized water (1.5 mL) was loaded into a 20-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 170°C for 4 days, and then cooled to room temperature naturally, initial pH 3.5, final pH 4.5. Yellow block crystals were isolated with minor unknown powder phase.

Synthesis of $(\text{Hbpi})_2[(\text{UO}_2)_4(\text{L})_6(\text{ox})_2]$ (HMPP-U4)

A mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50 mg, 0.1 mmol), HMPPA (17 mg, 0.1 mmol), bpi (10 mg, 0.045 mmol), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (20 μL), glycol (0.5 mL) and deionized water (1.5 mL) was loaded into a 20-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 170°C for 3 days, and then cooled to room temperature naturally, initial pH 3.5, final pH 5.0. Minor yellow block crystals were isolated from unidentified yellow powder phase.

Synthesis of $(\text{UO}_2)_2(\text{L})_2(\text{ox})(\text{bpbi})_2$ (HMPP-U5)

A mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50 mg, 0.1 mmol), HMPPA (17 mg, 0.1 mmol), bpbi (15 mg, 0.055 mmol), glycol (0.5 mL) and deionized water (1.5 mL) was loaded into a 20-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 170°C for 3 days, and then cooled to room temperature naturally, initial pH 2.5, final pH 4.0. Yellow block crystals were isolated.

X-ray crystallography

Suitable single crystals for title compounds were selected for single-crystal X-ray diffraction analyses. Crystallographic data were collected at 293 K on a Bruker Apex II CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT program.¹⁹ These structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL-97.²⁰ Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms associated with C and N atoms were placed by geometrical considerations and were added to the structure factor calculation. The hydrogen atoms on hydroxyl groups were not found in residual density map thus were added geometrically. **HMPP-U1** has one disordered OH group (O4), which was modeled satisfactorily by the PART command. ISOR command was used to constrain the atomic displacement parameters of some C and O atoms in **HMPP-U3** and **HMPP-U4**. A summary of the crystallographic data for these title complexes is listed in Table 1. Selected bond distances and angles are given in Table S1, ESI.† More details on the crystallographic studies are given in the ESI.†

Table 1. Crystal data and structure refinement for title complexes.

Compound	HMPP-U1	HMPP-U2	HMPP-U3	HMPP-U4	HMPP-U5
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Journal Name					
Empirical formula	C ₁₄ H ₁₆ O ₈ P ₂ U	C ₄₀ H ₄₂ N ₄ O ₁₆ P ₄ U ₂	C ₁₄ H ₁₃ N ₂ O ₇ PU	C ₇₆ H ₇₄ N ₄ O ₃₄ P ₆ U ₄	C ₂₇ H ₂₂ N ₂ O ₇ PU
Fw	612.24	1434.72	590.26	2725.33	755.47
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P2₁/c</i>	<i>P-1</i>	<i>P2₁/m</i>	<i>P2₁/n</i>	<i>P-1</i>
<i>a</i> /Å	9.8077(9)	9.382(2)	10.5513(7)	21.949(6)	8.946(6)
<i>b</i> /Å	5.5950(5)	11.204(3)	17.4551(11)	17.918(4)	11.706(7)
<i>c</i> /Å	16.0481(15)	12.243(3)	11.0376(7)	24.002(6)	13.404(8)
α /°	90	67.981(6)	90	90	87.195(10)
β /°	91.848(2)	85.397(6)	118.4590(10)	113.989(4)	76.239(12)
γ /°	90	71.885(6)	90	90	85.236(12)
<i>V</i> / Å ³	880.17(14)	1133.1(5)	1787.2(2)	8624(4)	1358.1(15)
<i>Z</i>	2	1	4	4	2
<i>F</i> (000)	572	682	1096	5152	722
ρ_{calcd} (Mg/m ³)	2.310	2.103	2.194	2.099	1.847
μ (Mo <i>K</i> α)/ mm ⁻¹	9.442	7.354	9.209	7.688	6.082
Collected / unique	4614 / 1739	7249 / 4499	10028 / 3686	43881 / 17065	7562 / 5343
<i>R</i> _{int}	0.0444	0.0462	0.0338	0.0724	0.0392
Gof	0.962	0.983	1.056	0.954	1.016
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0378 / 0.0774	0.0469 / 0.0802	0.0354 / 0.0966	0.0515 / 0.1140	0.0515 / 0.1123
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0777 / 0.0944	0.0626 / 0.0872	0.0514 / 0.1065	0.1119 / 0.1398	0.0703 / 0.1217

$$^a R_1 = \sum(\Delta F / \sum(F_o)) ; wR_2 = (\sum[w(F_o^2 - F_c^2)]) / \sum[w(F_o^2)^2]^{1/2}, w = 1/\sigma^2(F_o^2)$$

Results and discussion

Syntheses

Complex **HMPP-U1** was directly synthesized through hydrothermal reaction between HMPPA and UO₂²⁺ in 2:1 ratio. Further introduction of dib, layered structure of **HMPP-U2** was formed. When glycol was added, **HMPP-U3**, **HMPP-U4** and **HMPP-U5** with in-situ generated oxalate as coligand were formed. It is noted that either glycol or imidazoles could be the source of the oxalate anions. However, attempt to synthesize title uranyl phosphinate-oxalate compounds without adding glycol was a failure. This is a support of oxalate group in-situ generated through glycol.²¹ Further confirmation was approved that direct addition of oxalic acid could not result in title compounds.

Crystal structure of HMPP-U1

This compound crystallizes in a monoclinic space group *P2₁/c*. The asymmetric unit of **HMPP-U1** consists of half a crystallographically unique uranyl dication and one HMPP ligand (Fig. 1a). The UO₂²⁺ cation is equatorially coordinated by four O atoms from four phosphinate groups, forming a less common coordination environment of square plane bipyramid. The U=O distances in the axis are 1.76(7) Å, and the bond angle of O(1)=U(1)=O(1A) is 180°. The calculated bond-

valence sum for U(1) is 6.12, which is consistent with the formal valence of U(VI).²² The HMPP group serves as a bridge linking two uranyl cations with P-O-U connection (P(1)-O(2): 1.512(6) Å and P(1)-O(3): 1.516(6) Å). As a result, a one-dimensional chain-like structure is formed (Figure 1b). Such chains stack via weak $\pi \cdots \pi$ interactions (inter-centroid distance: 4.0 Å) to form the whole structure of **HMPP-U1** (Fig. 1c).

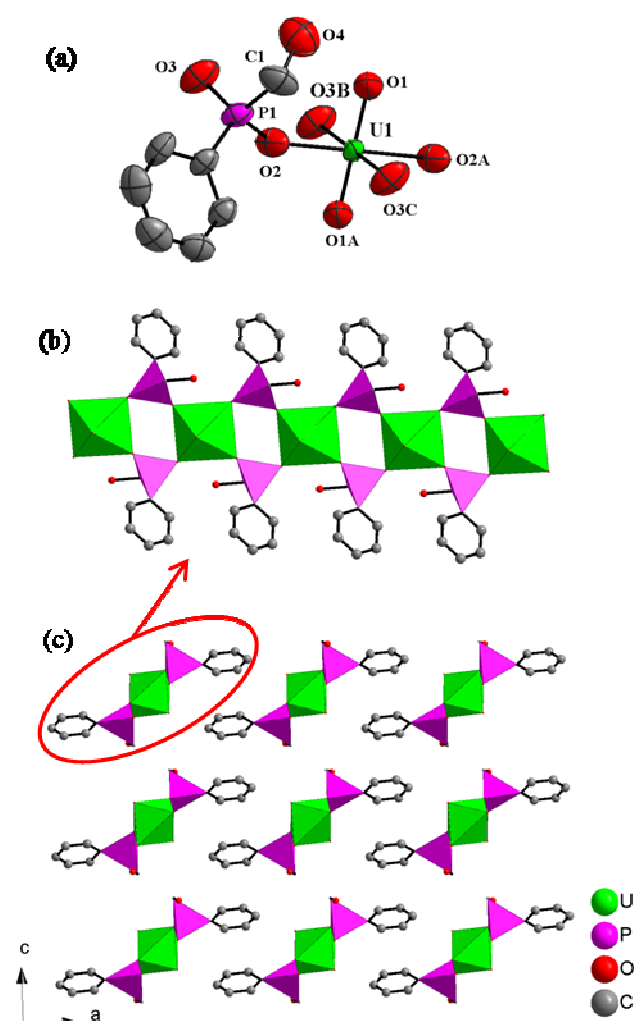


Fig. 1 (a) Coordination environment of **HMPP-U1**. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: A, 1-x, 1-y, 1-z; B, 1-x, -y, 1-z; C, x, 1+y, z. (b) Polyhedral view of structure of **HMPP-U1**. (c) The linear chain showing the connection between uranyl centers and the HMPP ligands.

Crystal structure of HMPP-U2

HMPP-U2 crystallizes in a triclinic space group $P-1$. Its asymmetric unit contains one uranium atom, two HMPP groups and half a dib molecule (Fig. 2a). The uranium atom is bound by two “y” oxo atoms along the axis with the U=O bond lengths of 1.761(5) and 1.775(5) Å. In the equatorial plane, it is coordinated by four oxygen atoms from four HMPP ligands and one nitrogen atom from the dib molecule. Thus a pentagonal bipyramidal surrounding of the uranium center is created. The U-O bond distances range from 2.328(6) to 2.361(5) Å. The U-N bond is longer with the distance of 2.546(6) Å. Each HMPP ligand bridges two uranyl centers, then a one-dimensional chain assembly similar to **HMPP-U1** is produced. The chains are pillared by dib via U-N connection, forming a two-dimensional layered arrangement of **HMPP-U2** (Fig. 2b). A view along c axis reveals the whole structure of **HMPP-U2** showing the packing of these layers (Fig. 2c).

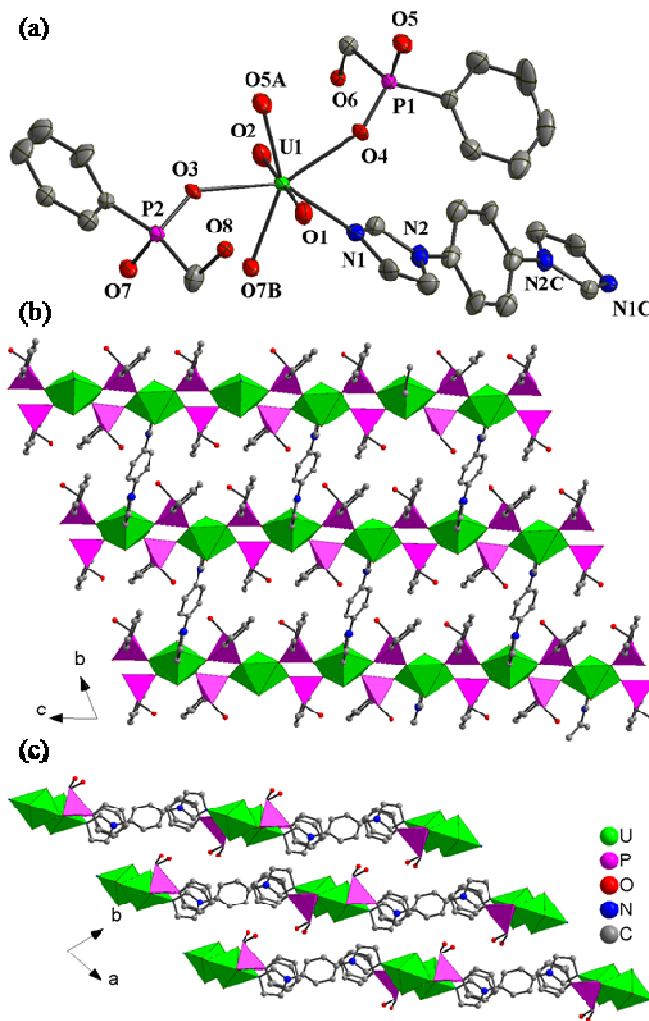


Fig. 2 (a) Coordination environment of **HMPP-U2**. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: A, 1-x, 1-y, 1-z; B, 1-x, 1-y, -z; C, -x, -y, 1-z. (b) The layered structure of **HMPP-U2** formed by uranyl polyhedra, HMPP and dib ligands. (c) Structural view of **HMPP-U2** showing the arrangement of the layers.

Crystal structure of HMPP-U3

It crystallizes in the monoclinic space group $P2_1/m$ and there are one uranyl cation, two HMPP ligands, one oxalate site and one dib site in its asymmetric unit (Fig. 3a). The uranium atom is in a pentagonal bipyramidal geometry defined by two axial oxo atoms, four O atoms from two HMPP ligands and one oxalate group, and one N atom from a dib molecule. The axial U=O bond lengths are 1.751(6) and 1.756(6) Å, the equatorial U-O distances range from 2.29(6) to 2.474(5) Å, and the U-N distance is 2.513(6) Å. Two UO_6N polyhedra are linked by chelate oxalate moiety, forming a uranyl dimer. Such uranyl dimers are connected by two unique HMPP ligands, producing a zigzag chain. The adjacent chains are pillared by dib molecules, generating a two-dimensional layered structure (Fig. 3b). As shown in Fig. 3c, close packing of such layers forms the whole structure of **HMPP-U3**.

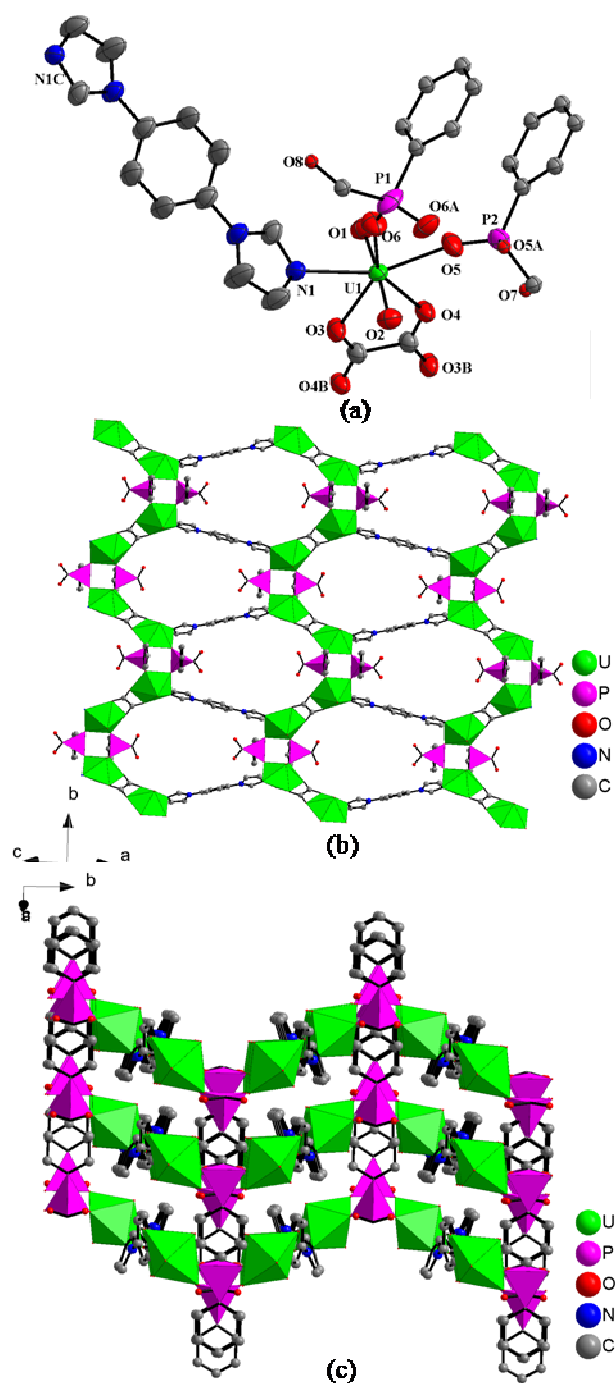


Fig. 3 Coordination environment of **HMPP-U3**. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: A, $x, 0.5-y, z$; B, $1-x, -y, 2-z$; C, $2-x, 1-y, 1-z$. (b). The layered assembly of **HMPP-U3** constructed by uranyl phosphinate linear chains linked by dib molecules. (c) Structural view of **HMPP-U3** showing the close packing of the layers.

Crystal structure of **HMPP-U4**

HMPP-U4 crystallizes in $P2_1/n$ space group. As shown in Fig. 4a, there are four unique uranium atoms, two oxalate and six HMPP ligands in its asymmetric unit. All the uranium atoms are seven-fold coordinated by oxygen atoms. The U=O distances along the axis are in the range of 1.732(8) ~ 1.766(7)

Å, whilst the U-O bond lengths in the equatorial plane are from 2.308(7) to 2.498(7) Å. U(1) and U(2) centers are chelated by an oxalate group forming a uranyl dimer. The same situation is for U(3) and U(4) ions. Every HMPP ligand bridges two dimeric uranyl building units, thus producing a similar one-dimensional species as in **HMPP-U3**. The chains are further joined by another HMPP groups to form the layered assembly of **HMPP-U4** (Fig. 4b). The whole structure of **HMPP-U4** is made up by the packing of such layers along c axis (Fig. 4c), whereas protonated bpi cations locate between the adjacent layers and interact with the layers through electrostatic cation/anion interactions. Besides, $\pi \cdots \pi$ interactions exist between the bpi molecules as well as between bpi and the HMPP groups. The inter-centroid distances of such interaction are in the range of 3.73 ~ 3.84 Å.

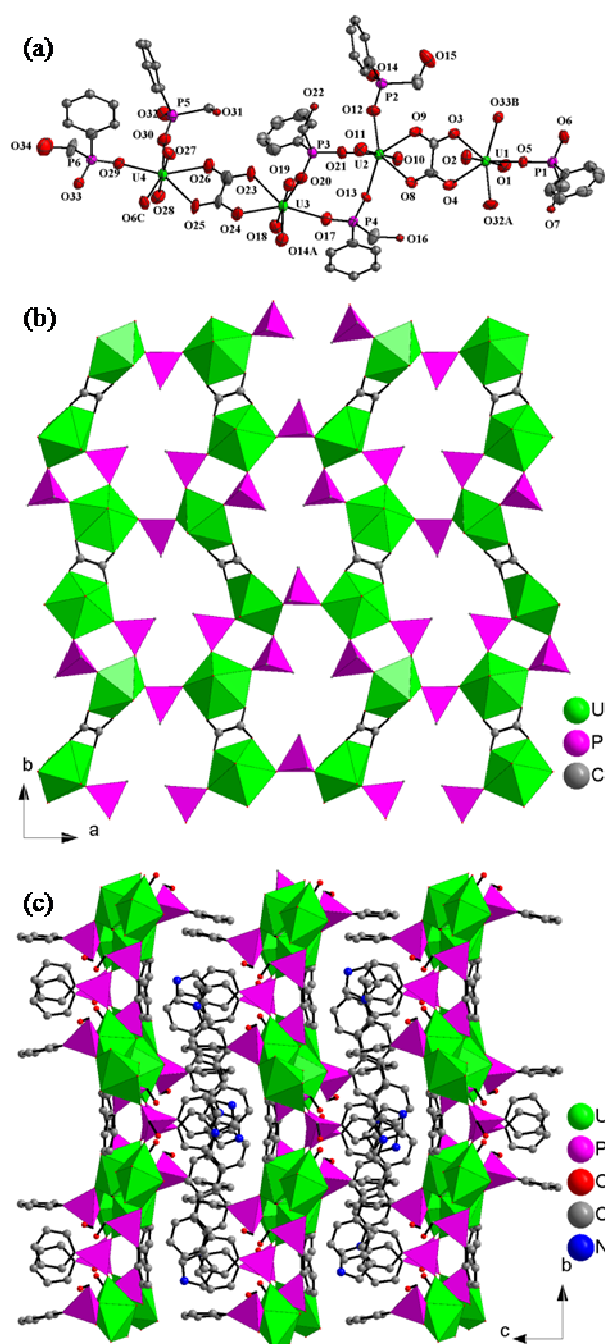


Fig. 4 (a) Coordination environment of **HMPP-U4**. Displacement ellipsoids are drawn at the 50% probability level. Template bpi is omitted for clarity. Symmetry codes: A, $1.5-x, 0.5+y, 1.5-z$; B, $1+x, y, z$; C, $-1+x, y, z$. (b) The layered structure of **HMPP-U4** formed by uranyl polyhedra, HMPP and oxalate ligands. The benzene ring of HMPP is deleted for clarity. (c) Structural view of **HMPP-U4** showing the arrangement of the layers with bpi molecules intercalation.

Crystal structure of **HMPP-U5**

This complex crystallizes in space group $P-1$, and contains one uranyl center, one HMPP ligand, half an oxalate and one bpbi co-ligand in its asymmetric unit (Fig. 5a). The uranyl center is five coordinated by four oxygen atoms and one N atom in the equatorial plane, in which two oxygen atoms come from two

HMPP ligands, two oxygen atoms from one oxalate group and the N atom from one bpbi co-ligand. The U-O distances range from 2.287(6) to 2.477(6) Å and the U-N bond length is slightly longer (2.562(8) Å). Two UO_5N pentagonal bipyramids are connected by an oxalate group and condense to a dimer. A similar chain structure like in **HMPP-U3** is constructed by connection of dimeric uranyl motifs and HMPP ligands. On the chain, the bpbi molecules are decorated via U-N connection (Fig. 5b). The whole structure of **HMPP-U5** is formed by stacking of such hybrid chains via π - π interaction with the inter-centroid distance of 4.07 Å. (Fig. 5c).

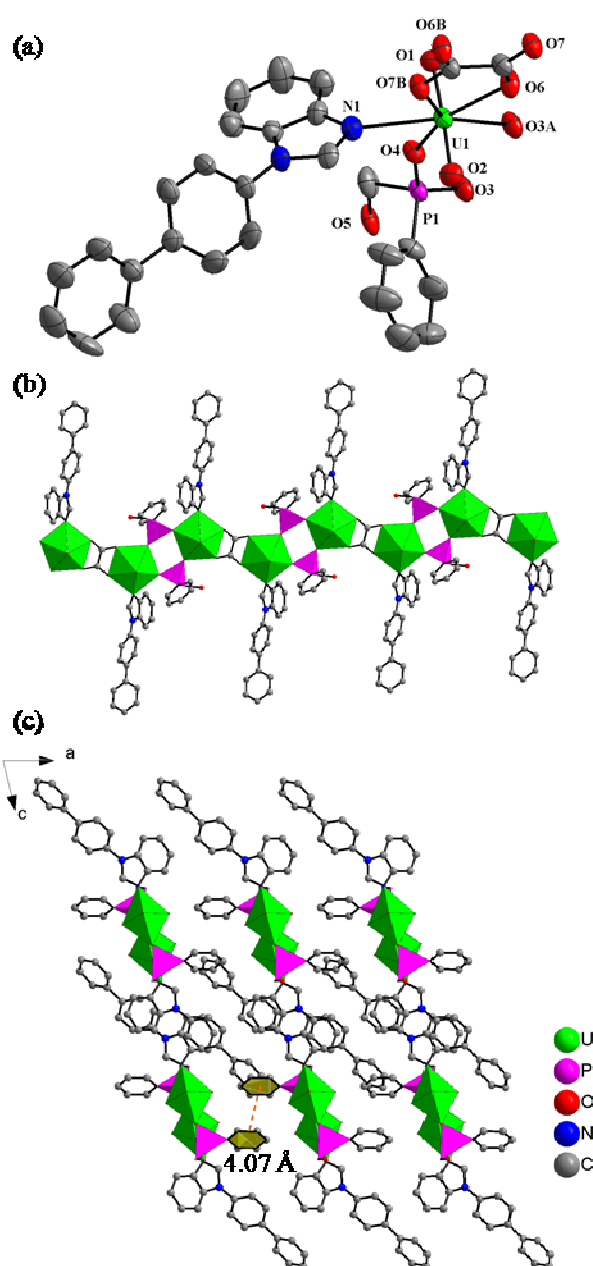


Fig. 5 (a) Coordination environment of **HMPP-U5**. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: A, $2-x, -y, 1-z$; B, $2-x, 1-y, 1-z$. (b) The one-dimensional structure of **HMPP-U5** with bpbi coordinated. (c) Structural view of **HMPP-U5** showing the arrangement of chains.

Structure Discussion

In **HMPP-U1** and **HMPP-U2**, mononuclear uranyl entities, UO_6 tetragonal and UO_6N pentagonal bipyramids, serve as building units, respectively, which are bridged by two HMPP ligands, forming similar chain assemblies. It is worth mentioning that when oxalate takes part in the construction of these uranyl phosphinates, a same dimeric uranyl motif connected by oxalate is involved in these uranyl phosphinates and interesting structural correlation is represented. In these complexes, the dimeric building units are linked by phosphinate ligands, forming a linear component. The dimeric unit is rotated along the chain with different degree in each compound (Fig. 6). As depicted in Table 2, the $\text{U}\cdots\text{U}$ distances of intra-dimeric unit are similar. While the linkage to next motif twists by different degrees, thus leading different periodic unit distances. In **HMPP-U3**, all the U atoms in the chain are in the same plane and the distance of a periodic unit is 12.215(8) Å. Such

chains are connected by dib with two N-donors, a two-dimensional layered structure of **HMPP-U3** is generated. If the chains are bridged by additional HMPP groups, a layered structure of **HMPP-U4** is constructed. The torsion angle of $\text{U}\cdots\text{U}\cdots\text{U}\cdots\text{U}$ in a repetitive unit is 144° , leading a longer periodic unit distance of 16.93(4) Å. For **HMPP-U5**, the uranyl centers also are arranged in a plane, but torsion angle of 180° in a periodic unit is featured. As a result, such chain is obviously elongated with the periodic unit length of 17.87(1) Å. Interestingly both bpi and bpbi possess one N-donor, in **HMPP-U4**, bpi molecules serves as templates, which are accommodated between the layers. In **HMPP-U5**, bpbi molecules are coordinated to the chain via U-N linkage, and terminate the further connection, leading one-dimensional architecture. Worthy of mention is that the organophosphinate ligand only features one coordination fashion with binding two U(VI) centers in these HMPP based uranyl complexes.

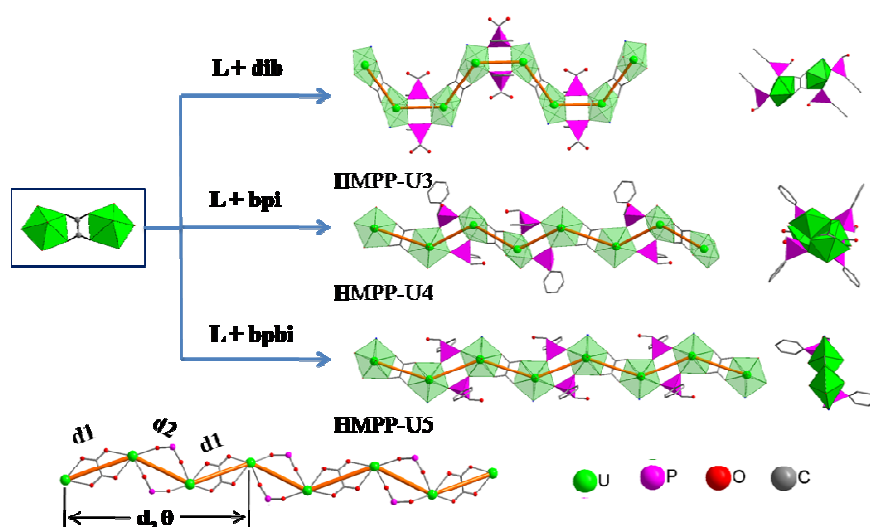


Fig. 6 The chain-like structures isolated from the uranyl-HMPP compounds. The common dimeric uranyl units rotate along the chain by different degree.

Table 2 Summary of distances of intra- and inter-dimeric motif ($\text{U}\cdots\text{U}$), distance and torsion angle of neighboring four U centers in the periodic unit of the chain ($\text{U}\cdots\text{U}\cdots\text{U}\cdots\text{U}$).

Complex	$d1/\text{Å}$	$d2/\text{Å}$	$d/\text{Å}$	$\theta/^\circ$
HMPP-U3	6.375(5)	5.239(5)	12.215(8)	0
HMPP-U4	6.42(1)	5.72(1)	16.93(4)	144
HMPP-U5	6.41(3)	6.07(3)	17.87(1)	180

IR spectroscopy

IR spectra of these synthesized uranyl organophosphinates are displayed in Fig. S3. The stretching vibrations of OH groups are indicated around 3350 cm^{-1} . The peaks around 2900 cm^{-1} are attributed to the CH_2 stretching modes. The stretching vibrations of carboxylate groups and the aromatic rings are indicated in the bands of $1650\text{--}1380\text{ cm}^{-1}$. The bands locating about 1100 cm^{-1} and in the low wavenumber region from 740 to 650 cm^{-1} are dominated by the O–P–O bending and P–C stretching vibrations. The symmetric stretching vibrations ν_1 of UO_2^{2+} are displayed in the range of $788\text{--}760\text{ cm}^{-1}$, while the

antisymmetric stretching modes ν_3 are observed in the area $930\text{--}852\text{ cm}^{-1}$.

Photoluminescent property

The emission of green light from uranyl-bearing compounds has been documented for decades. This charge-transfer based emission is always related to the symmetric and antisymmetric vibrational modes of the uranyl cation. Photoluminescent studies reveal that typical emission of green light with well-defined charge-transfer vibronic transitions is represented by **HMPP-U2** (Fig. 7). The spectrum consists of four emission peaks centered at 506, 527, 550 and 576 nm. These emissions correspond to the electronic and vibronic transitions $S_{11}\text{--}S_{00}$ and $S_{10}\text{--}S_{0v}$ ($v = 0\text{--}4$). Compared to the benchmark compound $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a red-shift of 17 nm is displayed. This difference may be due to the influence of coordination environment of uranyl center and organic ligands. For **HMPP-U1**, no representative emission from uranyl cation has been observed. In principle, not all uranyl complexes can exhibit fluorescence. The luminescence is related to many factors, such

as size and quality of the crystal, disorder within the equatorial plane of the uranyl group, organic ligands and so on.²³

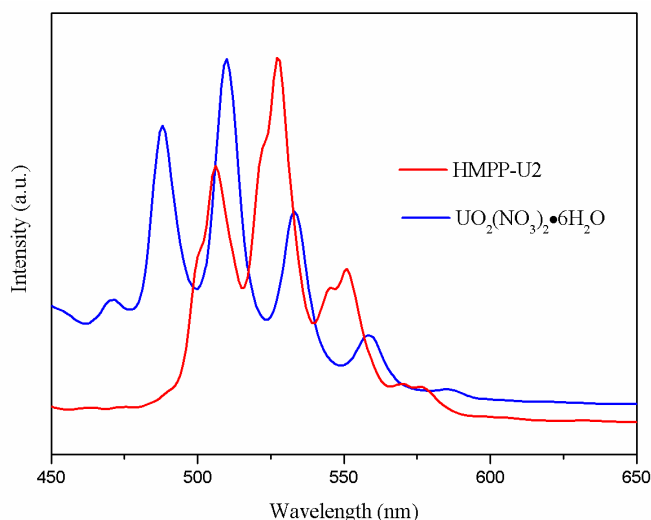


Fig.7 Emission spectra of **HMPP-U2** and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ showing the emission of green light.

Conclusions

In summary, a new series of uranyl organophosphinates has been isolated using hydroxymethyl phenylphosphinic acid as the ligand for the first time. **HMPP-U1** is a single chain structure formed by the connection of sole UO_6 square plane bipyramids and HMPP ligands. **HMPP-U2** exhibits layered structure constructed by UO_6N pentagonal bipyramids, HMPP and dib ligands. **HMPP-U3** also possesses layered arrangement, wherein a chain assembly formed by uranyl centers, HMPP and oxalate ligands is pillared by dib molecules. The two-dimensional structure of **HMPP-U4** is constructed by connection of UO_7 polyhedra and HMPP ligands. Protonated bpi species serve as space fillings and charge compensators between the interlayers. **HMPP-U5** features a one-dimensional assembly constructed by U-centered pentagonal bipyramids, HMPP and oxalate ligands, and bpbi molecules are coordinated to this chain via U-N connection. From **HMPP-U3** to **HMPP-U5**, the in-situ generated oxalate groups act as co-ligands to link the uranyl polyhedra, forming a common uranyl dimer. Such dimers are bridged by HMPP ligands, producing a one-dimensional arrangement, which is rotated differently and further linked by HMPP or imidazole derivatives, resulting in distinctive structures. In these complexes, the HMPP ligand only displays one coordination manner with binding two U centers. Future work will be seek to exploit new uranyl organophosphinates by adding hetero metal atoms as well as other auxiliary N-donor ligands.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Selected bond lengths and angles, powder X-ray diffraction patterns and the crystal data in CIF format (CCDC: 973714 for **HMPP-U1**, 1006856 for **HMPP-U2**, 973718 for **HMPP-U3**, 973716 for **HMPP-U4**, 973717 for **HMPP-U5**)]. See DOI: 10.1039/c000000x/

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